METHOD FOR ABATEMENT OF VOC IN EXHAUST GASES
BY WET PULSE CORONA DISCHARGE

CROSS-REFERENCE TO RELATED APPLICATION

This application claims priority from U.S. provisional application Serial No. 60/367,231 that was filed on March 25, 2002.

GOVERNMENTAL SUPPORT

The invention was made in the frame of a DOE sponsored project, Project Identification No. DE-FC07-00ID13868. The government has certain rights in the invention pursuant to that support.

DESCRIPTION

Low-temperature, non-equilibrium plasmas (also called "non-thermal" plasmas) are an emerging technology for abating diluting volatile organic compounds (VOC) emissions. These plasmas can be produced by a variety of electrical discharges or electron beams.

The basic feature of plasma technologies is that they produce plasma in which the majority of the electric energy (more than 99%) goes into production of energetic electrons, instead of heating the entire gas stream. These energetic electrons produce excited species, free radicals and ions) as well as additional electrons through the electron impact dissociation, excitation and ionization of the background molecules. These excited species, in turn, oxidize, reduce, or decompose the pollutant molecules.

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This mechanism of VOC removal is in contrast to the mechanism involved in thermal processes (such as plasma torches or furnaces, regenerative thermal oxidation (RTO) and several chemical techniques) that require heating the entire gas stream in order to destroy pollutants. In addition, the low-temperature plasma technology is highly selective and has relatively low maintenance requirements. Its high selectivity results in relatively low energy costs for emissions control while low maintenance keeps annual operating expenses low. Furthermore, these plasma discharges are very uniform and homogeneous (except gliding arcs), which results in high process productivity.

As mentioned above, RTO is more effective at high concentrations of VOC. Plasma is normally used at lower concentrations of VOC and in the cases where combustion is not effective, such as removal of nitrogen oxides (NO_x) or sulfur-containing compounds. Scrubbing of exhaust gases with water might be required for both techniques, but some plasma reactors can be designed as a single unit with a scrubber to reduce the equipment cost.

The gliding arc is a high-pressure gas discharge with high electron temperature and density and has been proposed for chemical gas processing [Lesueur et al., *J. de Physique* 51: C557-C564, 1990]. The arc starts in a narrow gap between two or more diverging electrodes in a gas flow when the electric field in this gap reaches approximately 3 kV/mm in air [Raizer, Gas Discharge Physics, Berlin, Springer-Verlag, 1997]. Then the arc current increases very rapidly, and the voltage on the arc drops. If the

gas flow is strong enough, it forces the arc to move along the diverging electrodes and to elongate.

The growing arc demands more power to sustain itself. At the moment when its resistance becomes equal to the total external resistance, the discharge consumes one-half of the power delivered by the source. This is the maximum power that can be transferred to the arc from the constant-voltage power supply. Next, the length continues increasing, but the supplied power is insufficient to balance the energy lost in heat transfer to the surrounding gas. The arc cools down and finally extinguishes. The next cycle starts immediately after the voltage reaches the breakdown value, usually just after the fading of the previous arc. (If the voltage is high enough, and the gap is very narrow, a new arc starts even before extinguishing of the old one [Pellerin et al., *J. Physics D-Applied Physics*, **33(19)**: 2407-2419, 2000]. A typical repetition rate of the arc is in the range from 10 Hz to 100 Hz and changes with the gas flow rate: the higher is the flow rate, the higher is the frequency.

Unlike regular high-current thermal arcs where both gas and electron temperatures (T and T_e) could be as high as 10000K, the low-current (from 0.1 to 1 A) gliding arcs are believed to operate in non-equilibrium regimes ($T < T_e$), and have low gas temperatures. The arc voltage could be as high as several kilovolts.' Typical vibrational and translational temperatures of the gas in a low-temperature gliding arc were measured to be respectively about 2000 – 3000K and 800 – 2100 K [Czernihowski et al., *Acta Physica Polonica A,* **89**: 595 -603, 1996]. Similar features are also intrinsic

for microwave discharges; showing that low-current gliding arcs could be definitely useful for plasma chemistry.

The physics of the gliding arc evolution is not well understood, especially the development of non-equilibrium conditions and stability at diminishing currents. Older models [Mutaf-Yardimci et al., *J. Applied Physics*, **87**: 1632-1641, 2000] did not account for variation of plasma conductivity and temperature during the gliding arc progress. This approach did not explain some recently discovered non-equilibrium effects in the low-current gliding arcs.

Mario Sobacchi [Sobacchi, M.G., "Hydrocarbon Processing in Non-equilibrium Gas Discharges", *Master of Science Thesis*, University of Illinois at Chicago, 2001] investigated the possibility of removal of specific chemical compounds with a low-current gliding arc discharge. A typical value of energy consumption for this discharge was 1 $kW \cdot hr/m^3$, when the targeted value was 0.02 $kW \cdot hr/m^3$. It was noted that non-uniformity of the discharge imposes certain difficulties to treat the gas efficiently. Experiments were performed using three different external resistance values; i.e., 25, 50, and 100 kW. The output voltage of the power supply was 10 kV, when the air flow rate ranged from 20 to 80 SLM.

Methanol (100 to 1000 ppm) was used as a substance to demonstrate viability of the gliding arc technology. In some runs, water was sprayed along the flow direction. It was found that at 20 SLM of air and independently of VOC concentration, all methanol was removed from the stream at power

consumption of 0.2 kW·hr/m³. No organic byproducts were detected by gas chromatography in the exhaust stream. The results were interpreted as encouraging, showing the possibility for further reduction of power consumption. Unfortunately, NO_x was detected in the exhaust at level of 3000 ppm, much exceeding all reasonable limits. It could be expected, however, that for more non-equilibrium arcs with lower currents or higher flow rates of air, the temperature of the arc channel will be lower, and reasonable levels of NO_x will be achieved.

Corona is a self-sustained electrical gas discharge that occurs only when the electric field is sharply non-uniform. The field near one or both the electrodes must be stronger than in the rest of the gap. This situation typically arises when the characteristic size r of the electrode to which the high voltage is applied, is much smaller than the inter-electrode distance d. If one considers a wire-into-cylinder configuration, the electric field in the space between the coaxial cylinders of radii r (internal cylinder) and R is given as a function of the radial coordinate x as:

$$E = \frac{V}{[x \ln(R/r)]}$$

where V is the voltage between the cylinders.

There is always some ionization in atmosphere due to high-energy particles coming from space. Existing electrons are accelerated by the electric field. They can ionize more molecules of the gas. New electrons are accelerated in the field, and so forth. Corona discharge occurs only when the value of the maximum electric field exceeds the

breakdown field. For coaxial cylinders, the critical electric field of corona ignition in air is expressed by an empirical formula suggested by Peek (1929):

$$E_c = 31\delta\left(1 + \frac{0.308}{\sqrt{\delta r}}\right) \ [\text{kV/cm}]$$

where δ is the ratio of air density to the density in standard pressure and temperature. It is clear that a constraint is imposed on the maximum field, which occurs on the surface of the sharp electrode, that is the high field or "corona carrying" electrode.

The formulae given above describe fairly well the physics of the corona with DC or slowly changing fields, such as in gas phase corona reactors (GPCR). For these applications, to be sustained at non-equilibrium state, the discharge can acquire only small power. Higher power would cause sparking and eventually lead to thermal arc formation.

Natural power limitations of DC corona technology gave rise to development of the pulsed corona technology. In a pulsed corona discharge, voltage is applied to the sharp electrode as a series of fast rising pulses. Incoming pulses generate a number of microdischarges (streamers); the faster the pulse, the more streamers are produced per unit length, increasing the power input per unit gas volume.

The width of the applied pulse must be minimized in order to avoid formation of spark discharge or thermalization of the streamers. For most geometries, then, the pulse rise time must be on the order of few nanoseconds and the duration of the pulse on the order of 100 ns.

The electron energy, in fact, depends on both the intensity of the electric field (i.e. on the voltage) and the mean free path. For a fast rising pulse, the mean electric field is very high (since the peak voltage is high), allowing the electrons to gain enough energy for the discharge to take place; however, since the duration of each pulse is much smaller than the interval between pulses, the mean required power is low (e.g., it is in the order of few Watts for the setups used for these experiments) even though the actual power of each single pulse is very high (about 1 MW). The negative polarity is predetermined by the existing equipment.

DC corona is a uniform discharge.. In contrary, the pulsed corona is highly non-uniform. All the discharge power is localized in streamers. To describe the physics of the discharge, one must consider a phenomenon of a streamer as a whole. Electromagnetic model of physics in streamers must be coupled with chemistry of excited species, and with internal particles (electrons, photons) transport. This coupling is very difficult because of enormous amount of computational work. Simplified models were developed, but they are still not adequate for the purposes of trustworthy chemistry prediction. Many parameters are known with great degree of uncertainty, such as electron cross-sections.

There are numerous methods for the waste gases treatments from volatile organic compounds (VOC) with the help of electrical discharges, and particularly with the help of the pulsed corona discharge [Malik et al., *Chinese J. Chem. Eng.*, 7(4) (1999)]. To remove one large VOC molecule with the help of such methods it is necessary to produce

several active radicals like OH. The energy price of
one radical production is very high - about 50 eV per
radical. As a result, total price of one VOC
molecule removal (transformation of VOC molecule into
H_2O and CO_2) is also very high - about 300 eV. It is
possible in this case to satisfy the industry demand
to spend not more than about 10 W-Hour/m^3 of the waste
gas only if VOC concentration is not higher than
about 30 ppm. Real industrial waste streams such as
that of the papermaking, metal cleaning and plating,
plastics manufacture and the like industries have VOC
contamination levels that are several times higher
(e.g., about 100 to about 6000 ppm), so usual plasma
methods for VOC removal are not applicable. .The
invention described hereinafter provides one method
by which the latter, more highly loaded exhaust gas
streams can be abated of VOC.

BRIEF SUMMARY OF THE INVENTION

The present invention contemplates a method
for treating exhaust gas streams that contain one or
more volatile organic compounds (VOC) to abate those
VOCs. A contemplated method for abatement of VOCs in
an exhaust gas stream comprises passing an exhaust
gas stream containing about 60 to about 6000 ppm VOC,
and more usually about 200 to about 3000 ppm, through
a pulsed corona discharge chamber in the presence of
a spray of water droplets or a flowing film of water
to form one or more oxidation products that dissolve
in the water spray droplets or film and provide an
effluent water stream and an effluent gas stream. In
the method, a contemplated pulsed corona discharges
at a rate of about 0.01 to about 2 kHz. The ratio of
the water spray rate to the exhaust gas flow is about

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0.2 to about 2 milliliters/minute at one standard
liter per minute of exhaust gas flow, and an
expenditure of not more than 50 eV per molecule of
VOC is utilized. This method provides a destruction
and removal efficiency of about 90 percent or more,
thereby abating the VOC. The method can operate at
substantially any temperature with the understanding
that lower temperatures typically provide slower
reaction rates.

In some preferred embodiments, the method
is utilized in part of a waste treatment system in
which the relatively small amount of water that
contains the dissolved oxidation products produced in
this method is admixed with the relatively larger
volume of industrial waste water produced by
papermaking, metal cleaning or plating process or
plastics manufacturing process. In another preferred
embodiment, the method is utilized after the gas
phase is contacted with water as a mist of particles
about 0.1 to about 1 millimeter in diameter or liquid
water to dissolve and thereby capture water-soluble
VOC such as methanol and acetone. The effluent gas
from such a pretreatment is then passed into the wet
pulsed corona discharge process discussed above with
the liquid phase being further subjected to
bioremediation or another type of purification
treatment. The gas phase produced from the above
process is passed over a gaseous sorbent (absorbent
and/or adsorbent) system such as activated charcoal
and vented to the air or passed into an air stream of
an incinerator or the like to eliminate vestigial VOC
that may have escaped elimination in a previous step.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a simplified schematic representation of the pulsed wet corona system of the present invention.

Figure 2 is a graphical representation of experimental results for destruction and removal efficiency (DRE) with using methanol as a model VOC in which percentage DRE is shown on the ordinate and water flow rate [milliliters per minute ml/min)] is shown on the abscissa.

Figure 3 is a graphical representation of experimental results for DRE using acetone as a model VOC, in which results are depicted as in Fig. 2.

Figure 4 is a graphical representation comparing the annualized costs in thousands of dollars (k$) versus plasma processing costs (watt-hours/cubic meter) for the present invention and a regenerative thermal oxidizer (RTO) of the prior art.

The present invention has several benefits and advantages.

One benefit is that high levels of VOC elimination efficiency can be obtained at relatively low start-up and running costs.

An advantage of the invention is that the products produced by the pulsed corona discharge reaction on the VOC are typically more soluble than are many of the VOC so that those materials can be more readily dissolved in the water flow that is used.

Another benefit of the invention is that the method and apparatus utilized are adaptable to being utilized with other air and water purification systems or methods.

Still further benefits and advantages of the invention will be apparent form the discussion that follows.

DETAILED DESCRIPTION OF THE INVENTION

A new method has been developed that combines the corona discharge with the scrubber to provide a "wet" corona discharge. [Fridman et al.,199th Meeting of the Electrochemical Society, Washington, March 25-29, 2001; Meeting Abstracts, Vol. 2001-1, Abstract No. 196; and Sobacchi et al., 15th International Symposium on Plasma Chemistry, Orleans, July 9-13, 2001, Symposium Proceedings, Vol. VII: Poster Contributions, pp. 3135-3140; Sobacchi, "Hydrocarbon Processing in Non-Equilibrium Gas Discharges", *Master of Science Thesis*, University of Illinois at Chicago, May 16, 2001; Kalashnikov, "Non-Equilibrium Gliding Arc And Corona Discharges For Abatement Of Volatile Organic Compounds", *Doctoral Thesis*, University of Illinois at Chicago, June 26, 2002.]

To obtain desirable VOC destruction with low energy consumption it is necessary to make proper design of pulsed corona discharge and scrubber. This method is applicable to substantially any existing waste gas stream that emanates from an industrial site such as a metal cleaning and plating, paint manufacturing, plastics manufacturing, petroleum refining and dye-making site that also includes a wastewater treatment facility for treating a waste water stream from a source other than the pulsed corona discharge.

The present invention contemplates a method for treating exhaust gas streams that contain one or

more volatile organic compounds (VOC) to abate those VOCs. Illustrative exhaust gas streams include, without limitation, those streams produced by papermaking, metal cleaning and plating, paint manufacturing, plastics manufacture, petroleum refining, dye-making and the like industries. In particular, a contemplated method is particularly useful in abating VOC produced in papermaking processes such as brownstock and oriented strandboard production (whose VOC are similar to those of papermaking), and particularly from the vents streams and dryer exhausts used in those processes.

A contemplated method for abatement of VOCs in an exhaust gas stream comprises passing an exhaust gas stream containing about 60 to about 6000 ppm VOC through a pulsed corona discharge chamber in the presence of a spray of water droplets or a flowing film of water to form one or more oxidation products that dissolve in the water spray droplets or film and provide an effluent water stream and an effluent gas stream. In the method, a contemplated pulsed corona discharges at a rate of about 0.01 to about 2 kHz, and more preferably about 0.1 to about 1 kHz. The ratio of the water spray or flow rate to the exhaust gas flow is about 0.2 to about 2 milliliters/minute at one standard liter per minute of exhaust gas flow, and an expenditure of not more than 50 eV per molecule of VOC is utilized. This method provides a destruction and removal efficiency of about 90 percent or more, to about 99 percent or more, thereby abating the VOC.

The method can operate at substantially any temperature with the understanding that lower temperatures typically provide slower reaction rates,

as is usually the case for chemical reactions. More typical temperatures of the exhaust gas stream are about 103° F (about 40° C) to about 150° F (about 65° C). Such temperatures are determined prior to entry into the pulsed corona discharge apparatus.

More usual and preferred VOC levels are about 200 to about 4200 ppm. More preferably still, those VOC levels are about 300 to about 3000 ppm.

Specific values of the water spray or flow rate and the exhaust gas flow volume can differ from one apparatus and gas stream to another. However, the ratio of water spray or flow rate to the exhaust gas flow is relatively constant at about 0.2 to about 2 milliliters/minute at one standard liter per minute (SLM) of exhaust gas flow. Thus, for wet corona discharge systems larger than that used illustratively herein, the water spray or flow rate can be on the order of gallons, liters or kiloliters per minute, with an accompanying increase in gas stream flow so that the ratio of the two corresponds to that noted above.

The contemplated method is illustrated herein in relation to a papermaking facility. The illustrative target exhaust gas streams for this invention such as high volume low concentration (HVLC) brownstock washer vent emissions can contain various VOCs in varying concentrations, as are seen in Table I, below.

Table I

Emitted VOC component	HVLC Brownstock Washer Vent Emissions according NCASI*	"worst case scenario" HVLC Brownstock Washer Vent Emissions suggested by GP**
Dimethyl Disulfide	2 ppm	20 ppm
Dimethyl Sulfide	-	1727 ppm
Methanol	83 ppm	2330 ppm
Acetone	3 ppm	-
Terpenes	209 ppm	62 ppm
Process Conditions		
Temperature	103°F	150°F
Relative Humidity	100%	100%

*NCASI = National Council for Air and Stream Improvement

**GP = Georgia Pacific

In the simplest case (shown schematically in Fig. 1) the wet corona setup permits for a water film to flow on the internal walls of the reactor. In a larger scalable geometry a water spray can be used instead of water film. Thus, the flow of water is scalable based on the size of the apparatus used, the VOC present in the exhaust gas, the volume of gas flow and other known or readily determined parameters that are associated with Henry's law and the equations discussed hereinafter.

While the present invention is susceptible of embodiment in various forms, there is shown in the drawings a number of presently preferred embodiments that are discussed in greater detail hereafter. It should be understood that the present disclosure is

to be considered as an exemplification of the present
invention, and is not intended to limit the invention
to the specific embodiments illustrated.

Referring to the drawings, a wet pulse
corona discharge system 10 is schematically
represented in Fig. 1. That figure shows a reactor
12 having internal walls 12a over which a water film
is permitted to flow. It will be understood by
persons having skill in the art that in a larger
scalable geometry a water spray can be used instead
of a flow, without departing from the novel scope of
the present invention. A corona discharge wire 14 is
provided within reactor 12. The reactor 12 and wire
14 create a wire-into-cylinder coaxial electrode
system 16. The inner, high voltage electrode 14 is,
in a preferred embodiment, a 0.5 mm diameter Inconel®
wire. The Inconel® alloy is selected for its
superior heat and oxidation resistance. It will,
however, be understood that other alloys or single
metallic element wires, can be used without departing
from the novel scope of the present invention.

The reactor vessel 12 creates an external
electrode 18, made up, in a preferred embodiment of
the present invention, of a 60 cm long cylindrical
glass tube 20 with an internal diameter 22, in a
preferred embodiment the diameter is 22.2 mm,
surrounded by a sheet of perforated metal 23. The
internal wall 20a of the glass tube 20 is covered by
a layer of absorbing material 24, which forms a
uniformly distributed water film in the reactor 12.

The tube 20 is held, in a preferred
embodiment, at the top by a Teflon® holder (not
shown) and at the bottom by a stainless steel holder
(not shown); stainless steel is preferred for the

bottom of the reactor to prevent deterioration of the holder itself due to the byproducts expected in the liquid phase, such as sulfuric acid. It will be understood that different materials can be utilized, both for the top and the bottom, without departing from the novel scope of the present invention. Further, it will be understood that either one or both of the materials noted above can be used either together or in other combinations without departing from the novel scope of the present invention. Preferably, materials having similar qualities, such as non-sticking and oxidation and reactivity free materials will be used for the materials of the top and bottom of the reactor.

The reactor 12 is sealed, in a preferred, by means of silicon O-rings (not shown).Although silicone O-rings are used in a preferred embodiment, it will be understood that O-rings of other materials, including rubber and plastic, can be used without departing from the novel scope of the present invention. The top holder (not shown) comprises the connections of the lines, which are schematically shown in Fig. 1, for the incoming water 30 and the outgoing (effluent) gas 32. In a preferred embodiment, water is introduced into the reactor 12 through sixteen, equally spaced holes with a diameter of $^1/_{32}$" (about 0.8 mm), to provide a uniform injection around the circular tube. It will be understood that any number of equally spaced holes, of various suitable diameters (either uniformly of the same diameter or of different diameters with suitable results) can be used to provide a uniform injection of water, without departing from the novel scope of the present invention.

The top holder (not shown) also contains the connection for the internal, high voltage electrode 14 and for the high voltage probe (shown schematically in Fig. 1). The bottom holder (not shown) includes threaded holes for the gas inlet 40 and for the water outlet (effluent) 42 (shown schematically in Fig. 1). To avoid any contact between this metal holder (not shown) and the high voltage (HV) electrode 14 and to prevent the formation of sparks, the wire 14 can be fixed to the holder (not shown) through a Teflon® insert (not shown), which completely contains the lower portion of the wire. As noted above, the type of insert described is a preferred embodiment and is not meant to limit the scope of the present invention.

Power is supplied, in a preferred embodiment, to the plasma source by a thyratron-based power supply 50, with 100 kΩ internal resistance and no-load voltage values from 0 to 20 kV. It will be understood that similar power supplies, having desirable power producing capabilities, can be utilized without departing from the novel scope of the present invention. In the preferred embodiment, pulses of about 100 ns duration and 10 ns rise time are applied and are transmitted to the central wire electrode 14 by means of a 50 Ω high-voltage, coaxial cable 52. The power of the plasma source is varied from 1 to 20 W by controlling the high voltage pulse amplitude and the pulse frequency, which could range from 0.01 to 2 kHz. Voltage is measured using a high voltage probe (not shown) such as model P6015A 1000X by Tektronik Inc., current measurements are performed, in a preferred embodiment, using a

standard current monitor such as current monitor #411 by Pearson Inc.

In the operation of the reactor 12 of the present invention, an electrode 14 is placed within glass tube 20, water is input into the system in such a manner that a film of water forms on the internal walls 12a of the reactor 12, simultaneously an exhaust gas stream containing VOC is introduced and the electrode is charged. The result includes the oxidation of VOC, their dissolution in the flowing water effluent and the release of gas phase byproducts in the gas effluent.

Correct choice of parameters should be based on theoretical estimations or experimental results. The solubility of a gas in water is described by the Henry's law, which states a relation between the concentrations of a gas in the liquid and in the gas phases. Usually, the Henry's law constant k_H is defined as:

$$k_H = \frac{c_a}{p_g} \qquad (1)$$

Here, c_a is the concentration of a species in the aqueous phase and p_g is the partial pressure of that species in the gas phase. The commonly used unit for the Henry constant is:

$$\left[\frac{M}{atm}\right] = \left[\frac{mol_{aq}/m_{aq}^3}{atm}\right] \qquad (2)$$

The higher the value of the Henry's law constant for a given compound, the higher the solubility of that compound in water. Values of the Henry's law constants for the VOCs of interest are shown in Table II, below. Oxidized compounds such as methanol, acetone and the intermediate byproducts from the oxidation of dimethylsulfide and α-pinene

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(that are the main substances from terpenes in HVLC brownstock washer vent emissions) appear to have a much higher solubility than the non-oxidized species.

Table II

Henry's law constant values

in standard conditions

Volatile Organic Compound	$k_H^\ominus \left[\dfrac{M}{atm} \right]$
Methanol CH_3OH	$2.2 \cdot 10^2$
Acetone CH_3COCH_3	$3.1 \cdot 10^1$
Dimethyl Sulfide CH_3SCH_3	$9 \cdot 10^{-1}$
α-Pinene $C_{10}H_{16}$	$4.9 \cdot 10^{-2}$
Butane C_4H_{10}	$1.2 \cdot 10^{-3}$
Sulfur Dioxide SO_2	$1.2 \cdot 10^1$

The solubility of a gas in water depends on the temperature. In reference to standard conditions ($T^\ominus = 298.15$ K), the Henry's constant is denoted as $k_H^\ominus$. Henry's law can be described as a function of temperature as:

$$k_H = k_H^\ominus \exp\left[\frac{-\Delta_{soln}H}{R}\left(\frac{1}{T} - \frac{1}{T^\ominus} \right) \right] \qquad (3)$$

where $\Delta_{soln}H$ is the enthalpy of solution.

A quasi two-dimensional model of VOCs absorption into water was developed. The model is based on the solution of the species conservation

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equations for the gas phase and for the liquid phase.
It yields to the following expression for the
destruction and removal efficiency (DRE):

$$DRE = \frac{(1-\alpha) \cdot e^{-\beta(1-\alpha)}}{1-\alpha \cdot e^{-\beta(1-\alpha)}} \qquad (4)$$

where β is the ratio between the convection time and
the diffusion time and can be written as:

$$\beta = \frac{4\tau_c}{\tau_d} = \frac{\left(D/d^2\right)}{\left(V_g/L\right)} \qquad (5)$$

with: D = diffusion coefficient in air;

                 d = electrode separation

     distance;

                 V_g = velocity of the gas;

                 L = length of the wet corona

     reactor; and

α is a ratio between gas and liquid flow rate that is
expressed as:

$$\alpha = \frac{Q_g}{Q_w V_{mol} k_H} \qquad (6)$$

with: Q_g = gas flow rate;

                 Q_w = water flow rate;

                 V_{mol} = gas volume per unit mole.

D and k_H are the only parameters related to the
specified compound whose removal is being analyzed;
the other factors describe the geometry of the
reactor (d and L) and the experimental conditions (V_g,
Q_g and Q_w).

    With the assumption, which holds true if
wet corona design is made appropriate, that the
convection time is much longer than the diffusion
time, i.e. $\beta \gg 1$, α becomes the critical parameter:
for $\alpha > 1$, the DRE is very low, whereas for $\alpha < 1$ high
values of DRE are obtained. Because the gas flow

rate is fixed for particular technology stream and V_{mol} and k_H are constant in standard conditions, assuming $\alpha = \alpha_{crit}=1$, a critical value for the water flow rate can be derived as:

$$Q_{w-crit} = \frac{Q_g}{V_{mol}k_H} \tag{7}$$

Only a flow rate higher than this critical value provides a high removal of a given substance by absorption into the water film. This theoretical analysis shows good agreement with the experimental results presented below.

Methanol removal by absorption into water was studied in the wet corona reactor. An initial concentration equal to 200 ppm of methanol was considered. Methanol is the most soluble among the organic compounds of interest, as Table II shows. The value of the critical water flow rate for absorbing methanol was calculated from the model to be Q_{w-crit} about 0.2 ml/min, in good agreement with the experimental results shown in Fig. 2. For a fairly low flow rate of the water film (about 0.9 ml/min), the DRE is almost complete (about 99.9%), suggesting that an optimal configuration in terms of the geometry of the reactor and of the ratio between gas and liquid flow rate has been obtained for the removal of methanol.

Acetone removal by absorption into water was studied for flow rate of the water film varying from zero to about 2 ml/min. The initial concentration of acetone in the gas stream was 200 ppm. For acetone, with a 1 SLM gas flow rate, the calculated value of the critical water flow rate is Q_{w-crit} about 1.3 ml/min, higher than for methanol, given the lower solubility in water; experimental

results, presented in Fig. 3, show good agreement with the theoretical calculations. A high removal efficiency (about 99%) can be reached using a fairly low water flow rate (about 2 ml/min).

Thus, absorption into water of compounds with high Henry's law constants, such as methanol and acetone, appears to be a very feasible solution given the low water flow rate required, which is, by weight, comparable to the gas flow rate or even lower; absorption is economically practical for the removal of these compounds from industrial gas streams when water is readily available (as in the case of the paper industry).

In accordance with a method of the invention, substantially all soluble VOC components, like methanol or acetone, are removed from the stream by water, and the only one radical OH produced by the pulsed corona discharge is used for treatment of one molecule of insoluble VOC, like dimethylsulfide.

Molecules of insoluble VOCs are non-polar; this is a reason of their very low solubility. After the interaction of OH radical with the molecule of insoluble VOC, this molecule transforms into a new molecule or radical, which is polar and more soluble. Then this more soluble substance is removed by the water stream of the scrubber. As a result not more than 50 eV per molecule of VOC is spent, and this system is applicable for the waste stream with higher level of contamination (about 200 ppm of insoluble VOC and any reasonable level of soluble VOC).

For example, in this system, one need only spend 10 W-Hour/m^3 for the waste gas treatment to reach 90% DRE for the case of the next VOC composition (Table 3).

Table 3

Gas composition tested in study

Ingredient	VOC content (ppm)
Dimethyl Sulfide	50
Methanol	200
Acetone	200
α-Pinene	50

During this study, the gas flow rate was 1 SLM, and water flow rate was 1.5 ml/min.

Usually, the radicals being dissolved in the water produce acidic solutions (pH < 7). Additionally, ozone molecules from the corona discharge also dissolve in the pulsed corona water flow to make it more acidic. As a result, the corona device is built from the materials that are stable to acidic solution: stainless steel, plastics, glass, carbon materials, and the like.

One basis for the application of the present invention to exhaust gases of paper industry or a similar industry is the presence of a huge amount of wastewater in this industry. As a result, a small amount of wastewater provided from the pulsed corona water flow does not create a problem; i.e., the pulsed corona wastewater flow can be mixed with the existing wastewater and the mix can be treated later according to the existing techniques. If at the particular plant the main wastewater is alkaline (pH > 7), an interaction of the pulsed corona wastewater with the main wastewater stream results in oxidation of the remaining dissolved VOC into H_2O and CO_2; i.e., in the waste mix water cleaning.

If the particular plant has the wastewater

that is of such quality that it can be used in spray systems and does not produce considerable amount of VOCs during spraying, this wastewater can be used in the corona discharge apparatus.

Currently, the regenerative thermal oxidizers (RTO) are used for VOC treatment in the paper industry [see, Harkness et al., NCASI Technical Bulletin No. 795, September (1999)]. These devises are very good for a high level of contamination, when VOC oxidation provides a substantial amount of energy. Otherwise, a lot of natural gas should be used for RTO operation. Other disadvantages of RTO are the SO_2 emission in the typical case of sulfur-contained VOC and cyclic operation resulting in cracking of the ceramic parts of RTO and high capital and operation expenses. The technology described herein is believed to be economical reasonable in the case of low energy consumption as can be seen from the annualized cost comparison between the Wet Corona and RTO processes shown in Fig. 4.

Each of the patents, applications, theses and articles cited herein is incorporated by reference. The use of the article "a" or "an" is intended to include one or more.

From the foregoing, it will be observed that numerous modifications and variations can be effected without departing from the true spirit and scope of the present invention. It is to be understood that no limitation with respect to the specific examples presented is intended or should be inferred. The disclosure is intended to cover by the appended claims modifications as fall within the scope of the claims.